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4 1 **Title**

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6 2 Hydrological process controls on nitrogen export during storm events in an agricultural  
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8 3 watershed

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40 17 Full-length paper

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**Abstract**

The dynamic characteristics of nitrogen (N) and suspended solids (SS) were investigated in stream water during four storm events in 2003 at the Shibetsu watershed, eastern Hokkaido, Japan. Analysis showed that total nitrogen (TN), nitrate-N ( $\text{NO}_3^-$ -N), dissolved organic nitrogen (DON), particulate nitrogen (PN), and SS concentrations all peaked sharply during the rising limb of the discharge hydrograph, but peaks of PN and SS were more significant than that of dissolved N. PN and SS consistently displayed clockwise hysteresis with higher concentrations during rising flows, whereas  $\text{NO}_3^-$ -N and DON showed different patterns among storms depending upon the antecedent soil moisture. An M (V) curve, defined as nutrient mass distribution vs. the volume of discharge, showed that a “first flush” of PN,  $\text{NO}_3^-$ -N, DON, and SS was observed, however, the distribution of nutrient loads in the discharge was different. PN and SS had a shorter flushing characteristic time constant ( $t_{1/e}$ , defined as the time interval required for a decline in nutrient concentrations in discharge water to  $e^{-1}$  (37% of their initial concentrations) but contributed 80% of fluxes during the first 50% of the discharge, while longer flush time ( $t_{1/e}$ ) of  $\text{NO}_3^-$ -N and DON with slowly decreased concentrations led to half loads during the recession of the discharge. These data indicated that the flush mechanisms might be distinguished between particulate nutrients and dissolved N. The analysis showed that concentrations of PN and SS derived from soil erosion were related to surface runoff. In contrast,  $\text{NO}_3^-$ -N originated from the near-surface soil layer associated with the rising shallow ground water table and mainly flushed with

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41 subsurface runoff. Different flushing mechanisms implied that different watershed best  
42 management practices should be undertaken for effectively mitigating water quality  
43 degradation.

44 **Key words:** first flush, flow paths, flushing, nitrogen, storm events.

For review

## 45 INTRODUCTION

46 Quantifying the export of N from catchments has become a significant issue for land  
47 managers over the past 20 years. Although many studies have demonstrated that the  
48 characteristics of nutrient export are complicated due to a variety of factors, such as  
49 geographic, hydrologic, climatic, biochemical, and anthropological factors and although  
50 each is not a fundamental process, they drew some conclusions in common. First, N  
51 export had a significant variable signal at a temporal scale. In particular, rainfall events  
52 and/or snowmelt seasons contributed to high concentrations and fluxes of N (Baron &  
53 Campbell 1997; Brooks & Williams 1999; Hatano *et al.* 2005; Inamdar *et al.* 2004;  
54 McNamara *et al.* 2008; Mitchell *et al.* 1996; Zhang *et al.* 2007). Second, the flushing of  
55 N during a snowmelt season or storm events was observed (Brown *et al.* 1999; Burns  
56 2005; Burns *et al.* 1998; Creed & Band 1998a, 1998b; Creed *et al.* 1996; Inamdar *et al.*  
57 2004; McHale *et al.* 2002; Zhang *et al.* 2007). Last, flow paths had a close relationship  
58 with N export (Jia *et al.* 2007; Jiang *et al.* 2008; Zhang *et al.* 2007).

59 There has been considerable interest in identifying the sources, flow paths, and  
60 transport mechanisms responsible for the export of N, especially  $\text{NO}_3^-$ -N, within  
61 watersheds at the seasonal and rainfall event scale. These studies have resulted in an  
62 improved understanding on some of the processes but many are not yet clearly  
63 understood. The mechanisms of  $\text{NO}_3^-$ -N export are usually explained by contradictory  
64 processes. Creed and Band (1998a, b) found a clockwise, discrete hysteresis pattern of  
65  $\text{NO}_3^-$ -N concentration from glaciated catchments in the Canadian Shield, and attributed

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4 66 this pattern to the flushing of  $\text{NO}_3^-$ -N from near-surface soil layers due to the rising of  
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6 67 groundwater table, but they didn't find any proof of the source of  $\text{NO}_3^-$ -N. In contrast,  
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8 68 Brown *et al.* (1999), Inamdar *et al.* (2004), and McHale *et al.* (2002) believed that  
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10 69  $\text{NO}_3^-$ -N export occurred via deep flow paths and the rise in  $\text{NO}_3^-$ -N concentrations were  
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12 70 associated with the rapid displacement of till water by infiltrating precipitation. Hill *et*  
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14 71 *al.* (1999) indicated that the biogeochemistry of the organic horizon could regulate the  
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16 72 patterns of  $\text{NO}_3^-$ -N loss in subsurface runoff movement by preferential flow pathways in  
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18 73 forest soils. Ocampo *et al.* (2006) explained that the dynamic of the shallow ephemeral  
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20 74 perched aquifer drove a shift from hydrological controls on  $\text{NO}_3^-$ -N discharge during the  
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22 75 "early flushing" stage to an apparent biogeochemical control on  $\text{NO}_3^-$ -N discharge  
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24 76 during the "steady decline" stage of the flushing response.  
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29 77 Less attention has been paid to dissolved organic N (DON) compared with  $\text{NO}_3^-$ -N.  
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31 78 Recent studies suggest that contributions of DON can be significant and constitute a  
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33 79 major portion of the total N solute export (Campbell *et al.* 2000; Willett *et al.* 2004).  
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35 80 Although stream nitrate and DON may originate from similar shallow subsurface and  
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37 81 surface flow paths during storm events, differences in flushing response among  $\text{NO}_3^-$ -N  
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39 82 and DON were found (Cooper *et al.* 2007; Sebestyen *et al.* 2008).  
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43 83 In spite of numerous investigations on N dynamics, studies on the relationship  
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45 84 between distribution of N fluxes and stream discharge in agricultural or forested  
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47 85 watersheds during storm events are scarce. Quantification of nutrient fluxes in sewage  
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49 86 systems and urban watersheds indicated that those watersheds presented strong "first  
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4 87 flush” for most storms and constituents (Barco *et al.* 2008; Bertrand-Krajewski *et al.*  
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6 88 1998; Lee *et al.* 2002). In general, the term “first flush” has been used to indicate that  
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9 89 the mass emission rate is higher during the initial portions of runoff than during the last  
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11 90 portion (Kondolf & Wilcock 1996; Lee *et al.* 2002). This characteristic of “first flush”  
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13 91 has been mentioned to define different pathways for particulate nutrients and dissolved  
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15 92 nutrients (Jiang *et al.* 2009) or to use for watershed best management practices (BMPs),  
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17 93 such as enhancement of sediment and nutrient removal efficiency by treating the first  
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19 94 stage of runoff using sedimentation devices or filters (i.e. ditches, tanks, and ponds)  
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21 95 (Barco *et al.* 2008).

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24 96 Several studies looked at the N export in Shibetsu watershed (Hayakawa *et al.* 2006;  
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26 97 Hayakawa *et al.* 2009; Nakata *et al.* 2008, unpublished data; Woli *et al.* 2004).  
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28 98 Hayakawa *et al.* (2009) reported that the net N input (NNI) amounted to 55 kg N ha<sup>-1</sup>  
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30 99 yr<sup>-1</sup> in the Shibetsu watershed and the N export from the watershed outlet accounted for  
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32 100 27% of the NNI. Some studies indicated that land use had a significant positive  
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34 101 correlation with NO<sub>3</sub><sup>-</sup>-N export and agricultural N was a dominant source (Hayakawa *et*  
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36 102 *al.* 2006; Woli *et al.* 2004). However, these studies do not focus on the mechanisms  
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38 103 controlling N export to streams at a high temporal resolution during storm events.  
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40 104 Therefore, this study highlights on the dynamic concentrations and flux distribution of  
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42 105 N in discharge during storms. The objectives of this study are to 1) assess the temporal  
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44 106 patterns of N concentrations during storm events, 2) evaluate the distribution of N  
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46 107 fluxes in discharge within a storm, 3) clarify whether the flushing of N-export exists  
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4 108 among  $\text{NO}_3^-$ -N, DON, and PN and what is the variation, and (4) examine the potential  
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6 109 sources of N export from the Shibetsu watershed.  
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## 8 110 **MATERIALS AND METHODS**

### 9 111 **Watershed description**

10 112 The Shibetsu watershed is located in eastern Hokkaido (outlet as shown in Fig. 1;  
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13 113 43.634N, 145.085E), Japan. The watershed area is 679 km<sup>2</sup>, and the upper parts  
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16 114 dominated by forest are covered by Volcanogenous Regosols, while the downstream  
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19 115 areas are mainly used for agricultural purposes and are covered by Cumulic Andosols,  
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22 116 Gray Lowland Soils, and Peat Soils. The topographical characteristic of the region has a  
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25 117 mean slope of 4.28° with a maximum value of 34°. The slopes are more gentle and  
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28 118 concave in downstream areas than that in upstream. This region has a hemi-boreal  
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31 119 climate, characterized by warm summers and cold winters. Precipitation averages 1147  
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34 120 mm yr<sup>-1</sup> and the annual mean temperature is 5°C, with the lowest mean monthly  
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37 121 temperature in February (-8.3°C) and the highest mean monthly temperature in August  
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40 122 (18.0°C) (1978-2002 average, Japan Meteorological Agency 2007,  
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43 123 <http://www.jma.go.jp>). The watershed consists of agriculture (51.4%), forest (45.6%),  
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46 124 urban area (1.4%), and waste land and road (1.6%). The Nakashibetsu town, covering  
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49 125 most of the Shibetsu watershed, has a large grassland area, and dairy farming is a main  
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52 126 occupation. The dominant vegetation in forest is Japanese larch-*Larix kaempferi*.  
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55 127 Grassland (covered by *Phleum pratense*) occupies more than 95% of the agricultural  
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58 128 land area, and the remaining is cultivated with maize (*Zea mays* L.), sugar beet  
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4 129 (*Saccharum officinarum*), potato (*Solanum tuberosum*), and Japanese radishes  
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6 130 (*Raphanus sativus* Linn.). The human population was estimated at 24000 persons (35  
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8 131 people km<sup>-2</sup>) concentrated in the middle part of the watershed.

#### 11 132 **Watershed monitoring, sampling, and analysis**

13 133 Base flow water samples were grabbed from the stream outlet in 1 L polypropylene  
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15 134 bottles once a month from March to November in 2003. An automated water sampler  
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17 135 (ISCO™ 3700) was installed at the outlet of Shibetsu watershed, and water samples  
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19 136 were collected during four storm events: June 20 (E1), July 11 (E2), September 30 (E3),  
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21 137 and October 23 (E4) in 2003. The auto-sampler was triggered when the rainfall was > 4  
22  
23 138 mm 30 min<sup>-1</sup> with intervals of 15 min to 1 h during the rising stage of discharge, while 2  
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25 139 to 6 h during the receding section. Water samples were transported to the laboratory  
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27 140 quickly after a storm and then stored at 4°C before analyses. Rainfall was measured by  
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29 141 a tipping-bucket rain gauge (0.2 mm) placed in an open area near the automated sampler.  
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31 142 Daily stream water stage measured every 10 min was obtained from the website of  
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33 143 Ministry of Land, Infrastructure and Transport, Japan (<http://www1.river.go.jp>).  
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35 144 Discharge was calculated using calibrated formulas based on the monitoring by local  
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37 145 government. Groundwater wells in near-stream forests were constructed of 5 cm (ID)  
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39 146 PVC pipes and groundwater levels were recorded using pressure transducer and  
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41 147 capacitance water level probes at 10 min intervals. A shallow groundwater well was  
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43 148 cored to the depth of 2.94 m under the ground surface where a coarse sandy sediment  
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45 149 layer was intersected. A deep groundwater well with a depth of 12.52 m was cored to  
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4 150 the aquifer of Mashu pumice layer. Soil samples were collected once in August 2008 at  
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6 151 27 sites representing most of the watershed area. Each sample was taken in triplicate  
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8 152 with an auger from depths of 0-20, 20-50, and 50-100 cm. The triplicate samples from  
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10 153 each depth were homogenized before analysis.

13 154 Suspended solids (SS) were measured from 800 ml subsamples that were filtered  
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15 155 through pre-weighed glass microfiber filters (47 mm, Whatman GF/F). The filters were  
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17 156 dried at 90°C for 24 h and weighed again. Total N (TN) was determined by the method  
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19 157 of alkaline persulfate digestion and HCl acidified UV detection. After filtering through  
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21 158 0.2  $\mu\text{m}$  membrane filters, water samples were used for analyzing total dissolved N  
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23 159 (TDN),  $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N,  $\text{NH}_4^+$ -N, and Si. Concentrations of TN and TDN were  
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25 160 determined by the method of alkaline persulfate digestion and HCl-acidified UV  
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27 161 detection.  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N were determined by ion chromatography (QIC Analyzer;  
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29 162 Dionex, Sunnyvale, CA);  $\text{NH}_4^+$ -N was determined by colorimetry using the indophenol  
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31 163 blue method; and Si was determined colorimetrically by the molybdenum blue method.  
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33 164 Particulate N (PN) and DON were calculated by subtracting the concentration of TDN  
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35 165 from TN, and inorganic N ( $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N,  $\text{NH}_4^+$ -N) from TDN, respectively. Soil  
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37 166 samples were air dried and ground to pass a 2 mm sieve for  $\text{NO}_3^-$ -N analysis.  $\text{NO}_3^-$ -N in  
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39 167 soil was extracted using a 1:5 soil:2 M KCl solution and the concentrations were  
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41 168 determined by colorimetry.

#### 47 169 **Data analysis**

49 170 For examining the variation in water chemistry, we performed Kruskal-Wallis test and  
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171 multiple comparisons by Steel-Dwass test.

172 *Antecedent precipitation index*

173 Several researchers have used relative antecedent precipitation index (API) values to  
174 compare soil moisture among pre-storm conditions (Christopher *et al.* 2008; Inamdar &  
175 Mitchell 2006; McDonnell *et al.* 1991). The API index was calculated for the four storm  
176 events in our study, which is defined as:

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$$API_x = \sum_{i=1}^x \frac{P_i}{i}$$

178 where  $x = 7$  and 21 days before a rain event and  $P_i$  (mm) is the total precipitation on the  
179  $i^{\text{th}}$  day before the event. We used  $API_7$  for calculating the surface soil moisture and  
180  $API_{21}$  for the deep groundwater situation, because the surface Volcanogenous soil  
181 usually has high infiltration rates and can quickly get into the shallow groundwater  
182 aquifer. But when the water seeps into deeper soil layer through the coarse sandy  
183 sediment layer, it needs longer time.

184 *Runoff coefficient*

185 The runoff coefficient is defined as the total volume of discharge divided by the total  
186 volume of precipitation (amount of precipitation multiplied by watershed area), which is  
187 another indicator of wetness in the watershed.

188 *Time constant*

189 A time series of discharge and the concentration of N in discharge highlight the export  
190 behavior of N from a watershed. We presumed an exponential decline in N  
191 concentrations during the receding limb of the discharge. According to Creed and Band

(1998a), this decline can be described by:

$$N_t = N_0 e^{-kt}$$

where  $N_t$  is the concentration of N in the discharge waters at time= $t$ , ( $\text{mg L}^{-1}$ ).  $N_0$  is the concentration of N in the discharge waters at  $t=0$ , the time that peak concentration of N is observed ( $\text{mg L}^{-1}$ ).  $t$  is time in h and  $k$  is the constant proportionality factor ( $\text{h}^{-1}$ ). A time constant ( $t_{1/e}$ ) is defined as the time interval that must elapse in order for the concentrations of N in the discharge waters to decline to  $e^{-1}$  (37%) of their initial concentration.

*M (V) curve and mass first flush ratio*

The M (V) curve, which is described as the normalized load ( $M_i$ ) vs. normalized water discharge volume ( $V_i$ ), was used to analyze the load distribution in discharge (Bertrand-Krajewski *et al.* 1998).

$$M_i = \frac{\sum_{i=1}^j C_i Q_i \Delta t_i}{\sum_{i=1}^N C_i Q_i \Delta t_i}, \quad V_i = \frac{\sum_{i=1}^j Q_i \Delta t_i}{\sum_{i=1}^N Q_i \Delta t_i}$$

where  $N$  is the total number of measurements,  $j$  is the index from 1 to  $N$ .  $C_i$  and  $Q_i$  are instantaneous concentration and water discharge. If the M (V) curve is above the bisector, “first flush” phenomenon occurs (Geiger 1987; Saget *et al.* 1995) and the magnitude of the first flush can be quantified for each storm and for each water quality parameter using a mass first flush (MFF) ratio (Barco *et al.*, 2008). The MFF ratio was calculated as:

$$MFF_n = \frac{M_i}{V_i}$$

where  $n$  is the index in the storm corresponding to the percentage of the water discharge, ranging from 0% to 100%. By definition, MFF ratio equals zero in the beginning of a storm and it always equals 1.0 at the end of the storm. The MFF ratio is a useful tool for quantifying first flush and can be statistically characterized or used in regressions or other investigations to understand the magnitude of a first flush and storm or catchment characteristics. For example, an  $MFF_{20}$  equal to 2.5 means that 50% of the mass is contained in the first 20% of the discharge water.

Additionally, measurements of the  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations in bulk rainfall samples during different storm events showed very low concentrations (i.e.  $\text{NO}_3^-$ -N was below  $0.15 \text{ mg L}^{-1}$ ;  $\text{NH}_4^+$ -N was below  $0.2 \text{ mg L}^{-1}$ ). Therefore, the atmospheric input of N with rainfall was not considered as an important source of stream water N during the hydrological events.

## RESULTS

### Hydrological storm events

The hydrological characteristics of the four storm events varied considerably (Table 1). The total amount of rainfall ranged from 50 mm to 91 mm. Although a single peak was observed for all events (Fig. 2), the peak discharges varied from  $51.4 \text{ m}^3 \text{ s}^{-1}$  to  $167.7 \text{ m}^3 \text{ s}^{-1}$  (Table 1). Fast hydrological response of the watershed to rainfall was reflected in the length of time to the peak ( $T_p$ , time from the start of rain to the peak of stream water discharge). The longest  $T_p$  was found in E2, which had the lowest antecedent

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4 232 precipitation index ( $API_7$ ) value (Table 1). In contrast, E3 with the highest antecedent  
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6 233 soil moisture (19.3 for  $API_7$  and 28.4 for  $API_{21}$ ) had the shortest  $T_p$  (Table 1). The  
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8 234 runoff coefficient increased with an increase in the value of  $API_{21}$ , except for E4; but it  
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10 235 also increased with the increase in groundwater level, except for E3, during four storms  
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12 236 from early summer to autumn (Table 1, Fig. 2), suggesting the antecedent soil moisture  
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14 237 together with the seasonal factors could have controlled the watershed wetness.

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17 238 The groundwater level in near-stream forests was analyzed since it might be critical  
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19 239 to describe evolution of solute signatures during the storm events. The focus here was  
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21 240 on the temporal response of groundwater level in near-stream forests vs. stream  
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23 241 discharge. The shallow and deep groundwater level along with discharge and  
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25 242 precipitation are presented in Fig. 2. Groundwater level during storm events indicated  
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27 243 surface saturation and deep seepage in the near-stream forests. Importantly, these water  
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29 244 levels showed that: (a) the maximum of shallow groundwater level just occurred at the  
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31 245 precipitation peak and before the stream discharge peak, implying the shallow  
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33 246 groundwater quickly responded to the rainfall and contributed to the stream discharge;  
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35 247 (b) deep groundwater was raising slowly at the rising limb of discharge, but kept  
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37 248 increasing after the recession of discharge; and (c) surface saturation was maintained  
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39 249 even after precipitation cessation and during the recession of discharge.

#### 40 41 42 43 44 250 **Comparison in N concentrations between storm events and base flow**

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47 251 Nutrients and SS concentrations in base flow were different among constituents (Table  
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49 252 2), The most prevalent form of N was  $NO_3^-$ -N (54% of TN, 59% of DTN, and 95% of  
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4 253 DIN). DON accounted for 36% of TN, and PN only 9% of TN. The concentrations  
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6 254 during storm events were highly variable among N species. The dominant form during  
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8 255 the storm events was not only  $\text{NO}_3^-$ -N but also PN.  $\text{NO}_3^-$ -N accounted for 8-70% of TN  
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10 256 with an average of 37%, 27%, 50%, and 45% for E1, E2, E3, and E4, respectively;  
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12 257 while PN accounted for 0-86% of TN depending primarily on the peak discharge, with  
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14 258 the average of 46%, 57%, 20%, and 21% for each storm event. The PN :  $\text{NO}_3^-$ -N ratio  
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16 259 ( Fig. 3) showed that PN was the dominant form on the rising limb of the discharge, and  
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18 260 an increase in rainfall amount increased the length of the dominant time (i.e. E2); while  
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20 261  $\text{NO}_3^-$ -N was dominant on the receding limb. DON ranked second ranging from 15 to  
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22 262 34% during the storm period.  $\text{NH}_4^+$ -N concentrations were very low as base flow, and  
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24 263 were below the detection limit in many samples. According to Kruskal-Wallis H and  
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26 264 Steel-Dwass test (Table 2), discharge, SS, PN, and  $\text{NH}_4^+$ -N all showed significant  
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28 265 difference among storm events and base flow. However,  $\text{NO}_3^-$ -N and DON only showed  
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30 266 difference among storm events; while TN didn't show any difference. In brief, the  
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32 267 concentrations of all forms of N (except for  $\text{NH}_4^+$ -N and  $\text{NO}_2^-$ -N) were significantly  
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34 268 higher than those observed in forested watersheds, regardless of the base flow or storm  
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36 269 events.  
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#### 42 **Dynamic concentrations of N during storm events**

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44 271 The concentrations of TN, PN, and SS changed notably and had similar patterns in all  
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46 272 storm events, which peaked sharply during the rising limb of discharge and then  
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48 273 dropped rapidly (Fig. 4). TN and PN concentrations are shown in Table 2 and Fig. 4. A  
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4 274 significant positive correlation was found between TN and PN ( $R^2=0.98$ ,  $p<0.001$ ). PN  
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6 275 and SS also had a significant positive correlation ( $R^2=0.89$ ,  $p<0.001$ ). The dissolved N  
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8 276 concentrations didn't show significant changes, although the peak concentrations also  
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10 277 occurred before the discharge peaked.  $\text{NO}_3^-$ -N concentrations varied slightly with  
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12 278 ranges of 0.5-0.8, 0.3-0.7, 0.5-1.0, and 0.4-0.8  $\text{mg L}^{-1}$ , while DON concentrations  
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14 279 ranged 0.1-0.6, 0.1-0.5, 0.2-0.8, and 0.3-0.7  $\text{mg L}^{-1}$  during the storms. The maximum  
15  
16 280 value of PN in E2 was much larger than those in other storm events, which could  
17  
18 281 probably be due to antecedent dry soil condition (low  $\text{API}_7$  value, Table 1).

22 282 The peaks of dissolved N followed the peaks of shallow groundwater level or after  
23  
24 283 the water table elevated to a certain level (Fig. 4). This corresponding response was  
25  
26 284 most obvious in E3, when concentrations of  $\text{NO}_3^-$ -N and DON both showed two peaks  
27  
28 285 corresponding to the shallow groundwater level hydrograph; while PN did not show the  
29  
30 286 second peak similar to dissolved N. Therefore we speculated that dissolve N was  
31  
32 287 sensitive to the change in shallow groundwater.

#### 35 288 **Discharge-concentration patterns and responses of N export during rising and** 36 37 289 **receding lamb of hydrograph**

40 290 Although N and SS all peaked before the discharge peaks, the relationships between  
41  
42 291 concentrations and discharge were different. PN and SS displayed consistently  
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44 292 clockwise hysteresis in all storm events, whereas dissolved N showed no consistent  
45  
46 293 pattern among storms. Counter-clockwise concentration-discharge relationships of  
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48 294  $\text{NO}_3^-$ -N and DON were found in E1, no hysteresis in E3, and clockwise hysteresis

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4 295 existed in E2 and E4 (Fig. 5).

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6 296 Discharge-weighted mean concentrations of nutrients and rainfall conditions during

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8 297 each rising section of period have been analyzed to investigate the runoff mechanisms.

9  
10 298 Table 3 shows that nutrient concentrations had significant positive correlation with the

11  
12 299 cumulative rainfall, whereas no uniform correlation with rainfall intensity in the storm

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14 300 events.

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16 301 As we observed that N and SS concentrations all peaked quickly during the rising

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18 302 section of discharge and declined during the receding section, we investigated the

19  
20 303 dynamic characteristics of concentrations during the receding limb of the discharge

21  
22 304 hydrograph to determine the flow path contributions in a catchment and potential N

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24 305 export affected by a storm event. The  $t_{1/e}$  values of PN and SS were shorter than

25  
26 306 dissolved N, and  $t_{1/e}$  for  $\text{NO}_3^-$ -N was the longest (Table 4). The reason could be that PN

27  
28 307 and SS were likely flushed away by overland flow and dissolved nutrients could have

29  
30 308 been removed by both surface and subsurface flow (Zhang *et al.* 2007). Moreover, we

31  
32 309 noticed that the  $t_{1/e}$  for all nutrients were longer in E1 than other storms and the longer

33  
34 310 time of export might have led to more loads of nitrate.

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36 311 **The M (V) curves of N loads distribution vs. discharge during storm events**

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38 312 The M (V) curve helps to understand the nutrient mass distribution vs. the water

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40 313 discharge volume relationship. Figure 6 shows the normalized loads of N and SS as a

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42 314 function of normalized discharge for the four storm events. All curves were above the

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44 315 bisector, which showed the “first flush” of constituents. The PN and SS curves were

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4 316 above the curves of  $\text{NO}_3^-$ -N and DON, indicating a stronger first flush for particulates,  
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6 317 probably because PN and SS associated with soil erosion were more prone to move  
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8 318 during the early stage of storm.

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10 319 In order to quantify the magnitude of first flush and analyze load distribution, the first  
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12 320 flush ratios ( $\text{MFF}_{30}$  and  $\text{MFF}_{50}$ ) were used. Table 5 shows that the  $\text{MFF}_n$  of PN and SS  
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14 321 were higher than that of  $\text{NO}_3^-$ -N and DON. On average,  $\text{NO}_3^-$ -N, DON, TN, PN and SS  
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16 322 transported 35%, 39%, 49%, 66%, and 71% of the total loads in the first 30% of the  
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18 323 water discharge during the four storms, respectively; and 56%, 63%, 70%, 80%, and  
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20 324 88% of loads for the first 50% of the water discharge. These data indicated that the first  
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22 325 flush of dissolved N was weaker than PN and SS and the contributions of first flush to  
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24 326 the export loads were different between particulate nutrients and dissolved N, which  
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26 327 might be ascribed to different flush mechanisms for the different forms of N in a  
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28 328 watershed.

### 33 329 **Contribution of storm events to annual N loads**

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35 330 We estimated the loads of N and SS during the storm events and found that TN  
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37 331 accounted for 27.7% and  $\text{NO}_3^-$ -N, DON, PN, and SS accounted for 16.2%, 24.7%,  
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39 332 45.4%, and 37.2%, respectively of the total annual loads during the four storms (Table  
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41 333 6). The largest storm, E2 with the lowest value of  $\text{API}_7$ , contributed the largest loads,  
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43 334 especially PN and SS.

## 44 335 **DISCUSSION**

### 45 336 **Impact of hydrologic characteristics**

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4 337 Antecedent soil moisture is one of the most important factors for watershed  
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6 338 hydrological response to rainfall. A previous study (Rusjan *et al.* 2008) showed that  
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8 339 higher API value could cause a faster hydrological response (shorter  $T_p$ ). Comparing the  
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10 340  $API_7$  and  $API_{21}$  values of our study, the value of  $API_7$  was more consistent with the  
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12 341 previous study, suggesting that the hydrological response depended more on the  
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14 342 antecedent soil moisture of shallow groundwater aquifer than the deep groundwater  
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16 343 level. But our study showed that the  $T_p$  was longer than other headwater streams  
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18 344 probably due to the bigger size of our watershed (Rusjan *et al.* 2008; Zhang *et al.* 2007,  
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20 345 2008). The shallow groundwater level showed that the saturation in near-stream areas  
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22 346 was dictated by antecedent moisture condition (i.e. ponding in E3 with highest API  
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24 347 value and antecedent groundwater level, Fig. 2; Table 1) and the shallow groundwater  
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26 348 might be recharged by subsurface flow and return flow from contributing hill slopes and  
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28 349 those flows were most likely responsible for the continued saturation of the near-stream  
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30 350 areas even after precipitation cessation and hydrograph recession (i.e. E1 and E2, Fig. 2).  
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32 351 Thus, subsurface flow could dominate the receding limb of the hydrograph and might  
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34 352 be a big contributor to  $NO_3^-$ -N export.  
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40 353 Runoff coefficient is another indicator of wetness in a watershed, which reflects not  
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42 354 only antecedent soil moisture, but also other factors such as evapotranspiration, growth  
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44 355 of vegetation, plant cover, etc. Our increasing values of runoff coefficient from summer  
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46 356 to autumn seemed to imply that the plant growth and evapotranspiration processes also  
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48 357 played an important role in watershed hydrological cycle, except for the increasing  
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4 358 groundwater level. The highest API and antecedent groundwater level both were  
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6 359 observed in E3, but the largest runoff coefficient was in E4. This might be related to the  
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8 360 decrease in water use by plants and evaporation in autumn.

10 361 Rainfall intensity was found to have negative correlation with  $\text{NO}_3^-$ -N, but a positive  
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12 362 correlation with PN (Zhang *et al.* 2008). However, there was no correlation between  
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14 363 nutrients and rainfall intensity in our study, probably owing to the lag of hydrological  
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16 364 response to rainfall (longer  $T_p$ , Table 1). The correlation between nutrient concentrations  
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18 365 and cumulative rainfall showed that the amount of rainfall was a controlling factor for  
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20 366 nutrient export in the Shibetsu watershed. To analyze the correlation between nutrient  
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22 367 concentrations and rainfall intensity, further monitoring needs to be conducted in the  
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24 368 headwater stream.

#### 28 29 369 **Major sources of PN, $\text{NO}_3^-$ -N, and DON**

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31 370 Temporal changes in stream chemistry reflect the sequence in which hydrological flow  
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33 371 paths link source areas to streams. As catchment wetness increases during storm events,  
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35 372 the nutrients in the stream reflect the sources that are available and the amount of water  
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37 373 that flows through the source areas of those nutrients. Although concentrations of  
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39 374  $\text{NO}_3^-$ -N, DON, and PN all were larger on the rising limb of the discharge hydrograph,  
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41 375 the differences including the export time, the export patterns, and the export load  
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43 376 distribution in the discharge imply that they could have resulted from different sources  
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45 377 with different export mechanisms.

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49 378 Previous studies have reported a significant positive correlation between nutrient  
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4 379 concentrations and discharge, and these relationships varied depending on study sites as  
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6 380 well as rain events (Ahearn *et al.* 2004; McNamara *et al.* 2008). Our study showed that  
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8 381 different patterns not only existed among storm events but also different nutrients at the  
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10 382 same study site, which implied a variation in a mechanism of nutrient export. PN  
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12 383 always with clockwise patterns and significant “first flush” indicated that it was mainly  
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14 384 sourced from the surface flow due to soil erosion, and a significant correlation with SS  
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16 385 could have been evidence. In contrast, the patterns of dissolved N were variable  
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18 386 associated with different shallow groundwater level or antecedent soil moisture, and the  
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20 387 “first flush” was very weak. Thus transport of dissolved N might be better related to  
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22 388 subsurface runoff or groundwater which is always affected by shallow aquifer or  
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24 389 antecedent soil moisture. Therefore, we speculated that PN could have been derived  
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26 390 from the surface soil while dissolved N appeared to be mainly transported by subsurface  
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28 391 flow or originated from groundwater.

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33 392 Inamdar *et al.* (2004) believed that  $\text{NO}_3^-$ -N export occurred via deep flow paths and  
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35 393 the rise in  $\text{NO}_3^-$ -N concentrations were associated with the rapid displacement of till  
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37 394 water by infiltrating precipitation, using base cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) as indicators.  
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39 395 McHale *et al.* (2002) and Iqbal (2002) also reached a similar conclusion. We used Si as  
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41 396 an indicator, which is regarded as only deriving from rock weathering in a deep layer,  
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43 397 and the result is shown in Fig. 7. An opposite trend was found between Si and  $\text{NO}_3^-$ -N  
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45 398 concentrations, which was different from the parallel trends (Inamdar *et al.* 2004),  
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47 399 implying that  $\text{NO}_3^-$ -N was not from deep groundwater; and the mechanism must differ  
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4 400 from the explanation of Inamdar *et al.* (2004).

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6 401 Creed and Band (1998a) attributed the early peaks in the  $\text{NO}_3^-$ -N concentration to the  
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8 402 “flushing” hypothesis, in which nutrients are leached from near-surface layers by a  
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10 403 rising water table followed by a quick lateral transport of these leached nutrients to the  
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12 404 stream via near-surface subsurface stormflow on the hillslope and/or surface, saturation  
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14 405 excess runoff in the riparian zone. Hydrologically, a key feature of this perceptual  
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16 406 model is full-column saturation of the soil profile or water table rises high enough into  
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18 407 the soil profile to encounter near-surface soils with high transmissivity and thus the  
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20 408 potential for significant lateral flow to occur. This ‘transmissivity feedback’ has now  
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22 409 become a common hypothesis to explain lateral flushing of labile nutrients (Bishop *et al.*  
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24 410 2004). In our study, we observed the shallow groundwater level to raise above 20 cm  
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26 411 depth under the soil surface during the storm events, and above ground surface at the  
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28 412 wet antecedent condition in E3 (Fig. 2). This indicates that the requirement of  
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30 413 hydrology for  $\text{NO}_3^-$ -N flushing was met in our study. In addition, a key requirement of  
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32 414 the “flushing” hypothesis biogeochemically also exists, that is the ready availability of  
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34 415 excess nutrients in the near surface soil horizons (Qualls & Haines 1991; Weiler &  
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36 416 McDonnell 2006). Previous studies found a highly significant positive correlation  
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38 417 between  $\text{NO}_3^-$ -N concentrations in stream water and the proportion of upland area in  
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40 418 Shibetsu watershed under a baseflow condition ( $r=0.89$ , Hayakawa *et al.* 2006;  $r=0.84$ ,  
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42 419 Woli *et al.* 2004), which indicated that the area of uplands was the most important  
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44 420 factor for determining  $\text{NO}_3^-$ -N concentrations. Woli *et al.* (2004) also stated that the  
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4 421 regression coefficient had a significant positive correlation with the cropland surplus N,  
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6 422 chemical fertilizer N, and manure fertilizer N. Meanwhile, our soil chemical analysis  
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8 423 revealed that  $\text{NO}_3^-$ -N concentration in 0-20 cm depth of soil layer was significantly  
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10 424 higher than that of 20-50 cm and 50-100 cm depths (Fig. 8). These studies above all  
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12 425 indicated that the higher N application rates resulted in the greater field surplus N  
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14 426 accumulated in the top 0-20 cm soil layer and had the potential to leach into the stream  
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16 427 in the Shibetsu watershed. In addition, local famers usually apply fertilizer on  
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18 428 grasslands in spring and summer, and apply manure in spring or autumn (the annual  
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20 429 application rate of chemical fertilizer N is  $80 \text{ kg ha}^{-1}$  and an equal amount of manure  
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22 430 fertilizer N is added, Agricultural Department of Hokkaido Government, 2002), which  
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24 431 had a high risk of  $\text{NO}_3^-$ -N leaching during the rainy seasons if fertilizer management  
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26 432 was not appropriate (Jia *et al.* 2007). Thus, we believe that the source area of  $\text{NO}_3^-$ -N  
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28 433 flushing was variable in the near-surface soil layer in upland areas due to the rising  
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30 434 shallow groundwater level. Shallow groundwater level consistently reached a maximum  
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32 435 (closest to the soil surface) before peak of  $\text{NO}_3^-$ -N concentration and discharge (Fig. 4)  
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34 436 thus supporting the flushing of  $\text{NO}_3^-$ -N.  
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40 437 On the basis of the variable source area (VSA) concept, for a given watershed, N  
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42 438 flushing may have been regulated not by the total VSA but by the rate of change in the  
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44 439 expanding source area ( $dVSA/dt$ ). Although the rate that would have been regulated by  
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47 440 topography (Creed & Band 1998a), we believe that the rate also may be regulated by  
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49 441 antecedent shallow groundwater level which affects the water connectivity of the  
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4 442 watershed in a rain event and may lead to a different  $dVSA/dt$ . For example, E1 needs  
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6 443 longer time to connect the hydraulic connectivity well because of the shallow  
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8 444 groundwater level and dry antecedent soil moisture, which makes  $NO_3^-$ -N flux moving  
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10 445 slower from the variable source areas at the first stage (smaller values of  $dVSA/dt$ ). This  
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13 446 may be one of the reasons to explain the counterclockwise direction of the hysteresis  
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15 447 loops of E1 as a “prolonged flushing mechanism” (Weiler & McDonnell 2006; Rusjan  
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18 448 *et al.* 2008).

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20 449 A similar pattern of concentrations between DON and  $NO_3^-$ -N in all storm events  
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22 450 was observed in our study (Fig. 9). Several studies found the DON peaks on the rising  
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24 451 limb similar to our finding (Buffam *et al.* 2001; Hill 1999; Inamdar & Mitchell 2007;  
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26 452 McHale *et al.* 2000; Vanderbilt *et al.* 2003). However, Vanderbilt *et al.* (2003) attributed  
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28 453 this pattern to the flushing of decomposing leaf litter; Inamdar and Mitchell (2007) and  
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30 454 Hill (1999) reported that the stream DON were derived from throughfall. In contrast,  
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32 455 Hagedorn *et al.* (2000, 2001) found DON peaks on the recession limb and attributed this  
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34 456 to mobilization of DON during its passage through the forest canopy and organic-rich  
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36 457 topsoil. In the case of Shibestu watershed, we just found the DON peaked after a  
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38 458 maximum value of shallow groundwater level and the trends of DON and shallow  
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40 459 ground water level were very similar, especially in E3 (Fig. 9). Therefore, we speculate  
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42 460 that it may correlate with ground water rising, and that it may lead to flushing just like  
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44 461  $NO_3^-$ -N. However, we have no evidence to confirm the source of DON, owing to the  
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46 462 lack of analyses of throughfall, litter, and soil water. However, we noticed that the  
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4 463 concentrations of DON in E3 and E4 (in autumn) were significantly higher than that in  
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6 464 E1 and E2 (Table 2). Hagedorn *et al.* (2001) attributed the high DON exports to  
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8 465 elevated decomposer activity and availability of fresh leaf litter in fall. While Hayakawa  
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10 466 *et al.* (2006) reported a positive relationship between upland area (grassland area) and  
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12 467 DON concentrations in the Shibetsu watershed. Decomposing of grass litter and manure  
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14 468 application in autumn could be the reason for the relationship. Thus our finding may  
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16 469 confirm the flushing of decomposed leaf litter on the forest and decomposed manure  
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18 470 and leaf litter on the grassland.  
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#### 21 22 471 **Implication of the “first flush” for watershed management**

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24 472 Two observations about the “first flush effect” in our study may have important  
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26 473 implication for the management of water resources: (1) high concentrations and fluxes  
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28 474 of SS and PN exported rapidly for a short time at the beginning of discharge; and (2)  
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30 475 slow recession of nitrate concentration and long flushing time in the falling limb lead to  
31  
32 476 half of the  $\text{NO}_3^-$ -N flux export. The higher initial SS and PN concentrations early in the  
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34 477 runoff that are associated with a first flush have important interaction with the removal  
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36 478 efficiency of the best management practice (BMP). It has been noted that many BMPs,  
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38 479 such as ponds and wetlands, operate at great efficiency in removing particles including  
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40 480 PN during storm events if the pond or wetlands can effectively reduce the nutrients that  
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42 481 are transported at the rising limb of discharge during the first flush (Luo 2008). Gentle  
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44 482 sloping landform has the potential to last long time of water retention; and agricultural  
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46 483 landscapes have typically been found to leach greater amounts of  $\text{NO}_3^-$ -N (Hayakawa *et*  
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4 484 *al.* 2006; Woli *et al.* 2004). Geologic characteristics associated with agricultural  
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6 485 operations in Shibetsu watershed might lead to a long flushing time of  $\text{NO}_3^-$ -N, which  
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8 486 would likely contribute to a much higher  $\text{NO}_3^-$ -N concentration and flux to the water  
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10 487 body. Thus appropriate fertilizer management in summer and autumn in the Shibetsu  
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12 488 watershed, where the rainfall is rich during these seasons, is apparently crucial for  
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14 489 preventing excess N losses to stream during storm events. In addition, Hayakawa *et al.*  
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16 490 (2006) studied the impact of wetland on  $\text{NO}_3^-$ -N concentration by comparing Shibetsu  
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18 491 watershed with another wetland watershed and found that wetland played an important  
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20 492 role in attenuation of  $\text{NO}_3^-$ -N. The spatial distribution of wetland or riparian areas in the  
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22 493 watershed and their connectedness with the stream network will be a key for delivery of  
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24 494  $\text{NO}_3^-$ -N and thus regulate the flushing response. However, this application must be  
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26 495 carefully undertaken because the regulation of wetlands or riparian forests on  $\text{NO}_3^-$ -N  
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28 496 flushing is complicated (Inamdar & Mitchell 2006).

### 497 **Conclusions**

498 Although concentrations of N and SS all peaked at the rising limb of discharge, PN and  
499 SS consistently displayed clockwise hysteresis between concentration and discharge and  
500 showed a short flush time constant ( $t_{1/e}$ ), while dissolved N showed long  $t_{1/e}$  and  
501 different patterns among storms associated with antecedent soil moisture. These  
502 differences indicated that particulate N originated from the surface soil and was  
503 transported by surface flow. In contrast, dissolved N was related to subsurface flow.  
504  $\text{NO}_3^-$ -N was leached from near-surface soil layers by rising water table followed by a

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4 505 quick lateral transport of the leached  $\text{NO}_3^-$ -N to the stream via subsurface flow on the  
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6 506 cropland. Although concentration patterns of DON and  $\text{NO}_3^-$ -N were similar, DON  
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8 507 could have been closely related to the ground water rising and decomposed leaf litter  
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10 508 and manure. Further study is required to take throughfall, litter, and soil water into  
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12 509 consideration.

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15 510 Although the first flush of N and SS were observed, PN and SS were more significant  
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17 511 and contributed 80% of fluxes at the first 50% of the discharge, whereas dissolved N  
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19 512 with slowly decreased concentrations led half loads to export during the recession of the  
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21 513 discharge. The different flushing mechanisms between particulate nutrients and  
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23 514 dissolved N implied that different BMPs should be conducted for effective mitigation of  
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26 515 N export on a watershed scale.  
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26 527 [Japan.](#)

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33 529 **REFERENCES**

- 34  
35 530 Ahearn DS, Sheibley RW, Dahlgren RA, Keller KE 2004: Temporal dynamics of stream  
36  
37 531 water chemistry in the last free-flowing river draining the western Sierra Nevada,  
38  
39 532 California. *J. hydrol.* **295**, 47-63.  
40  
41 533 Agricultural Department of Hokkaido Government. Standard fertilizer application for  
42  
43 534 Hokkaido 2002; Sapporo (in Japanese).  
44  
45 535 Barco J, Papiri S, Stenstrom MK 2008: First flush in a combined sewer system.  
46  
47 536 *Chemosphere* **71**, 827–833.  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 537 Baron JS, Campbell DH 1997: Nitrogen fluxes in high elevation Colorado Rocky  
5  
6 538 Mountain Basin. *Hydrol. Process.* **11**, 783–799.  
7  
8  
9 539 Bertrand-Krajewski J-L, Chebbo G, Saget A 1998: Distribution of pollutant mass vs  
10  
11 540 volume in storm water discharges and the first flush phenomenon. *Water Res.* **32**  
12  
13 541 **(8)**, 2341–2356.  
14  
15 542 Bishop K, Seibert J, Kohler S, Laudon H 2004: Resolving the double paradox of rapidly  
16  
17 543 mobilized old water with highly variable responses in runoff chemistry. *Hydrol.*  
18  
19 544 *Process.* **18 (1)**, 185–189.  
20  
21  
22 545 Brooks PD, Williams MW 1999: Snowpack controls on nitrogen cycling and export  
23  
24 546 seasonally snow-covered catchments. *Hydrol. Process.* **13**, 2177–2190.  
25  
26  
27 547 Brown VA, McDonnell JJ, Burns DA, Kendall C 1999: The role of event water, a rapid  
28  
29 548 shallow flow component, and catchment size in summer stormflow. *J. Hydrol.* **217**,  
30  
31 549 171–190.  
32  
33 550 Buffam I, Galloway JN, Blum LK, McGlathery KJ 2001: A stormflow/baseflow  
34  
35 551 comparison of dissolved organic matter concentrations and bioavailability in an  
36  
37 552 Appalachian stream, *Biogeochemistry* **53**, 269–306.  
38  
39  
40 553 Burns DA, Hooper RP, McDonnell JJ, Freer JE, Kendall C, Beven K 1998: Base cation  
41  
42 554 concentrations in subsurface flow from a forested hillslope: the role of flushing  
43  
44 555 frequency. *Water Resour. Res.* **34**, 3535–3544.  
45  
46  
47 556 Burns DA 2005: What do hydrologists mean when they use the term flushing? *Hydrol.*  
48  
49 557 *Process.* **19**, 1325–1327.  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 558 Campbell JL, Hornbeck JW, McDowell WH, Buso DC, Shanley J B, Likens GE 2000:  
5  
6 559 Dissolved organic nitrogen budgets for upland forested ecosystems in New  
7  
8 560 England, *Biogeochemistry* **49**, 123– 142.
- 10 561 Christopher SF, Mitchell MJ, McHale MR, Boyer EW, Burns DA, Kendall C 2008:  
11  
12 562 Factors controlling nitrogen release from two forested catchments with contrasting  
13  
14 563 hydrochemical responses. *Hydrol. Process.* **22**, 46–62
- 17 564 Cooper R, Thoss V, Watson H 2007: Factors influencing the release of dissolved  
18  
19 565 organic carbon and dissolved forms of nitrogen from a small upland headwater  
20  
21 566 during autumn runoff events. *Hydrol. Process.* **21**, 622–633
- 24 567 Creed IF, Band LE, Foster NW *et al.* 1996: Regulation of nitrite-N release from  
25  
26 568 temperate forest: a test of N flushing hypothesis. *Water Resour. Res.* **32**,  
27  
28 569 3337-3354.
- 31 570 Creed IF, Band LE 1998a: Export of nitrogen from catchments within a temperate forest:  
32  
33 571 evidence for a unifying mechanism regulated by variable source area dynamics.  
34  
35 572 *Water Resour. Res.* **11**, 3105–3120.
- 38 573 Creed IF, Band LE 1998b: exporting functional similarity in the export of nitrite-N from  
39  
40 574 forested catchments: a mechanistic modeling approach. *Water Recour. Res.* **34**,  
41  
42 575 3079-3093.
- 44 576 Geiger W 1987: Flushing effects in combined sewer systems. In: Proceedings of the 4th  
45  
46 577 International Conference Urban Drainage, Lausanne, Switzerland, pp. 40–46.
- 49 578 Hagedorn F, Bucher J, Schleppe P 2001: Contrasting dynamics of dissolved inorganic  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 579 and organic nitrogen in soil and surface waters of forested catchments with  
5  
6 580 Gleysols. *Geoderma* **100**, 173–192.  
7  
8  
9 581 Hagedorn F, Schleppi P, Waldner P, Fluhler H 2000: Export of dissolved organic  
10  
11 582 carbon and nitrogen from Gleysol dominated catchments—The significance of  
12  
13 583 water flow paths. *Biogeochemistry* **50**, 137–161.  
14  
15 584 Hatano R, Nagumo T, Hata H *et al.* 2005: Impact of nitrogen cycling on stream water  
16  
17 585 quality in a basin associated with forest, grassland and animal husbandry,  
18  
19 586 Hokkaido, Japan. *Ecol. Eng.* **24**, 509–515.  
20  
21  
22 587 Hayakawa A, Shimizu MK, Woli KP, Kuramochi K, Hatano R 2006: Evaluating Stream  
23  
24 588 Water Quality through Land Use Analysis in Two Grassland Catchments: Impact  
25  
26 589 of Wetlands on Stream Nitrogen Concentration. *J. Environ. Qual.* **35**, 617–627.  
27  
28  
29 590 Hayakawa A, Woli KP, Shimizu M, Nomaru K, Kuramochi K, Hatano R 2009: The  
30  
31 591 nitrogen budget and relationships with riverine nitrogen exports of a dairy cattle  
32  
33 592 farming catchment in eastern Hokkaido, Japan. *Soil Sci. Plant Nutr.*, In press.  
34  
35  
36 593 Hill AR, Kemp WA, Buttle JM, Goodyear D 1999: Nitrogen chemistry of subsurface  
37  
38 594 storm runoff on forested Canadian Shield hillslopes. *Water Resour. Res.* **35**,  
39  
40 595 811-821  
41  
42  
43 596 Inamdar SP, Mitchell MJ 2006: Hydrologic and topographic controls on storm-event  
44  
45 597 exports of dissolved organic carbon (DOC) and nitrate across catchment scales.  
46  
47 598 *Water Resour. Res.* **42**, W03421, doi: 10.1029/2005WR004212.  
48  
49 599 Inamdar SP, Mitchell MJ 2007: Storm event exports of dissolved organic nitrogen  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 600 (DON) across multiple catchments in a glaciated forested watershed. *J. Geophys.*  
5  
6 601 *Res.* **112**, G02014, doi:10.1029/2006JG000309.  
7  
8  
9 602 Inamdar SP, Christopher SF, Mitchell MJ 2004: Export mechanisms for dissolved  
10  
11 603 organic carbon and nitrate during storm events in a glaciated forested catchment in  
12  
13 604 New York, USA. *Hydrol. Process.* **18**, 2651–2661.  
14  
15 605 Iqbal MZ 2002: Nitrate flux from aquifer storage in excess of baseflow contribution  
16  
17 606 during a rain event. *Water Res.* **36**, 788–792.  
18  
19  
20 607 Jia HY, Lei AL, Lei JS, *et al.* 2007: Effects of hydrological processes on nitrogen loss  
21  
22 608 in purple soil. *Agr. Water Manage.* **89**, 89–97.  
23  
24 609 Jiang R, Zhu B, Tang JL, Luo ZX, Wang D, Xin W, Wei SQ 2008: Characteristics of  
25  
26 610 nitrogen and phosphorus losses in typical rainfall-runoff events in a small  
27  
28 611 watershed in hilly area of purple soil. *Journal of Agro-Environment Science* **27(4)**,  
29  
30 612 1353-1358 (in Chinese with English summary).  
31  
32  
33 613 Jiang R, Zhu B, Tang JL, Luo ZX 2009: Transportation processes and loss fluxes of  
34  
35 614 nitrogen and phosphorous through storm runoff in a typical small watershed in the  
36  
37 615 hilly area of purple soil. *Journal of hydraulic engineering* **40(6)**, 659-666 (in  
38  
39 616 Chinese with English summary).  
40  
41  
42 617 Kondolf GM, Wilcock PR 1996: The flushing flow problem: defining and evaluating  
43  
44 618 objectives. *Water Resour. Res.* **32**, 2589–2600.  
45  
46  
47 619 Lee JH, Bang KW, Ketchum LH, Choe JS, Yu MJ 2002: First flush analysis of urban  
48  
49 620 storm runoff. *Sci. Total Environ.* **293 (1-3)**, 163-175.  
50  
51  
52  
53  
54  
55  
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58  
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60

- 1  
2  
3  
4 621 Luo ZX 2008: Stormwater runoff pollution and its control mechanism of natural ditch in  
5  
6 622 a rural township—a case study of Linshan rural township in the hilly area of purple  
7  
8 623 soils, China. PhD dissertation of Chinese Academy of Sciences (in Chinese with  
9  
10 624 English abstract).
- 11  
12  
13 625 McDonnell J, Owens IF, Stewart MK 1991: A case study of shallow flow paths in a  
14  
15 626 steep zero-order basin. *Water Resour. Bull.* **27**, 679–685.
- 16  
17 627 McHale MR, Mitchell MJ, McDonnell JJ, Cirimo CP 2000: Nitrogen solutes in an  
18  
19 628 Adirondack watershed: Importance of dissolved organic nitrogen, *Biogeochemistry*  
20  
21 629 **48(2)**, 165–184, doi:10.1023/A:1006121828108.
- 22  
23  
24 630 McHale M, McDonnell JJ, Mitchell MJ, Cirimo CP 2002: A field based study of soil-  
25  
26 631 and groundwater nitrate release in an Adirondack forested watershed. *Water*  
27  
28 632 *Resour. Res.* **38(4)**, 1029/2000 WR000102.
- 29  
30  
31 633 McNamara JP, Kane DL, Hobbie JE *et al.* 2008: Hydrologic and biogeochemical  
32  
33 634 controls on the spatial and temporal patterns of nitrogen and phosphorus in the  
34  
35 635 Kuparuk River, arctic Alaska. *Hydrol. Process.* **22**, 3294–3309.
- 36  
37  
38 636 Mitchell MJ, Raynal DJ, Driscoll CT 1996: Biogeochemistry of a forested watershed in  
39  
40 637 the central Adirondack Mountains: temporal changes and mass balances. *Water,*  
41  
42 638 *Air, and Soil Pollut.* **88**, 355–369.
- 43  
44  
45 639 Ocampo CJ, Oldham CE, Sivapalan M, *et al.* 2006: hydrological versus biogeochemical  
46  
47 640 controls on catchment nitrate export: a test of the flushing mechanism. *Hydrol.*  
48  
49 641 *Process.* **20**, 4269–4286  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 642 Ohte N, Tokuchi N, Katsuyama M, Hobara S, Asano Y, Koba K 2003: Episodic  
5  
6 643 increase in nitrate concentrations in streamwater due to the partial dieback of a  
7  
8 644 pine forest in Japan: runoff generation processes control seasonality. *Hydrol.*  
9  
10 645 *process.* **17**, 237-249.  
11  
12 646 Qualls RG, Haines BL 1991: Geochemistry of dissolved organic nutrients in water  
13  
14 647 percolating through a forest ecosystem. *Soil Sci. Soc. Am. J.* **55**, 1112–1123.  
15  
16 648 Rusjan S, Brilly M, Mikos M 2008: Flushing of nitrate from a forested watershed: An  
17  
18 649 insight into hydrological nitrate mobilization mechanisms through seasonal  
19  
20 650 high-frequency stream nitrate dynamics. *J. Hydrol.* **354**, 187– 202  
21  
22 651 Saget A, Chebbo G, Bertrand-Krajewski J 1995: The first flush in sewer system. In:  
23  
24 652 Proceedings of the 4th International Conference Sewer Solids-Characteristics,  
25  
26 653 Movement, Effects and Control, Dundee, UK, pp. 58–65.  
27  
28 654 Sebestyen, SD, Boyer EW, Shanley JB, Kendall C, Doctor DH, Aiken GR, Ohte N 2008:  
29  
30 655 Sources, transformations, and hydrological processes that control stream nitrate  
31  
32 656 and dissolved organic matter concentrations during snowmelt in an upland forest,  
33  
34 657 *Water Resour. Res.* **44**, W12410, doi: 10.1029/2008WR006983.  
35  
36 658 Vanderbilt KL, Lajtha K, Swanson FJ 2003: Biogeochemistry of unpolluted forested  
37  
38 659 watersheds in the Oregon Cascades: Temporal patterns of precipitation and stream  
39  
40 660 nitrogen fluxes, *Biogeochemistry* **62**, 87– 117.  
41  
42 661 Weiler M, McDonnell JJ 2006: Testing nutrient flushing hypotheses at the hillslope  
43  
44 662 scale: a virtual experiment approach. *J. Hydrol.* **319**, 339–356.  
45  
46  
47  
48  
49  
50  
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54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 663 Willett VB, Reynolds BA, Stevens PA, Ormerod SJ, Jones DL 2004: Dissolved organic  
5  
6 664 nitrogen regulation in freshwaters, *J. Environ. Qual.* **33**, 201– 209.  
7  
8  
9 665 Woli, KP, NagumoT, Kuramochi K, Hatano R 2004: Evaluating river water quality  
10  
11 666 through land use analysis and N budget approaches in livestock farming areas. *Sci.*  
12  
13 667 *Total Environ.* **329**, 61–74.  
14  
15 668 Zhang Z, Fukushima T, Onda Y *et al.* 2007: Nutrient runoff from forested watersheds in  
16  
17 669 central Japan during typhoon storms: implications for understanding runoff  
18  
19  
20 670 mechanisms during storm events. *Hydrol. Process.* **21**, 1167–1178  
21  
22 671 Zhang Z, Fukushima T, Onda Y, *et al.* 2008: Characterisation of diffuse pollutions from  
23  
24 672 forested watersheds in Japan during storm events — its association with rainfall  
25  
26  
27 673 and watershed features. *Sci. Total Environ.* **390**, 215-226.  
28  
29  
30  
31  
32  
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35  
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4 674 **Figure legends**

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6 675 **Figure 1** Location of the study watershed and water sampling site.

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8 676 **Figure 2** Precipitation, stream discharge, and ground water level (only one well is  
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10 677 shown, the others are similar) during storm events in 2003.

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12 678 **Figure 3** The ratio of PN:  $\text{NO}_3^-$ -N during storm events.

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15 679 **Figure 4** Temporal changes in N and SS concentrations, discharge, rainfall, and shallow  
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17 680 groundwater level during storm events.

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20 681 **Figure 5** Patterns of N and SS during storm events. Arrows indicate the time course.

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22 682 **Figure 6** M (V) curve: normalized mass first flush relative to normalized discharge.

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24 683 **Figure 7** Concentrations of Si and  $\text{NO}_3^-$ -N during storm events.

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26 684 **Figure 8**  $\text{NO}_3^-$ -N concentrations in soil profile (ANOVA,  $p < 0.05$ ,  $n = 27$ ).

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29 685 **Figure 9** Concentrations of  $\text{NO}_3^-$ -N and DON, and shallow ground water level during  
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31 686 storm events.

686 **Table 1** Characteristics of each hydrological storm event in the study area

Storm event	Date	Precipitation		Rainfall duration (h)	<sup>a</sup> API <sub>k</sub>		Discharge			% of annual discharge	Runoff coefficient
		Total	Max		API <sub>7</sub>	API <sub>21</sub>	Total	Peak	<sup>b</sup> T <sub>p</sub>		
		(mm)	(mm h <sup>-1</sup> )	(×10 <sup>6</sup> m <sup>3</sup> )			(m <sup>3</sup> s <sup>-1</sup> )	(h)			
E1	2003/6/20-2003/6/23	80	11	16	3.2	5.2	10.6	51.4	14	1.31	0.195
E2	2003/7/11-2003/7/14	91	11	23	0.0	6.6	53.8	167.7	16	6.65	0.870
E3	2003/9/30-2003/10/3	55	15	15	19.3	28.4	39.1	122.6	9	4.83	1.047
E4	2003/10/23-2003/10/25	50	8	19	1.9	2.6	38.6	135.8	11	4.77	1.136

<sup>a</sup> API<sub>k</sub>: Antecedent precipitation index determined for 7 and 14 preceding days.

<sup>b</sup> T<sub>p</sub>: Time to peak (the time from the outset of rain to the peak of stream water discharge)

E1, E2, E3, and E4 represent the storm events on June 20, July 11, September 30, and October 23 in 2003, respectively.

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688 **Table 2** Discharge, SS, and N concentrations during the storm and base flow events.  
 689 Different superscript letters (a, b, and c) followed by median values indicate significant  
 690 difference (Steel-Dwass test,  $p < 0.05$ )

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Storm events		Discharge ( $\text{m}^3 \text{ s}^{-1}$ )	SS ( $\text{mg L}^{-1}$ )	$\text{NO}_3\text{-N}$ ( $\text{mg L}^{-1}$ )	TN ( $\text{mg L}^{-1}$ )	DON ( $\text{mg L}^{-1}$ )	PN ( $\text{mg L}^{-1}$ )	$\text{NH}_4\text{-N}$ ( $\text{mg L}^{-1}$ )	$\text{NO}_3\text{-N}$ /TN(%)	DON /TN(%)	PN /TN(%)
E1	Mean	32.0	34.1	0.6	1.7	0.3	0.8	0.006	37	16	46
	Median	28.1 <sup>a</sup>	15.7 <sup>bc</sup>	0.5 <sup>a</sup>	1.5 <sup>a</sup>	0.2 <sup>a</sup>	0.6 <sup>a</sup>	0.002 <sup>bc</sup>			
	Min	22.6	6.8	0.5	1.0	0.1	0.3	0.0			
	Max	51.4	141.7	0.8	3.8	0.6	2.7	0.02			
E2	Mean	64.8	327.9	0.5	2.7	0.3	1.9	0.009	27	15	57
	Median	50.2 <sup>b</sup>	81.5 <sup>b</sup>	0.4 <sup>b</sup>	1.6 <sup>a</sup>	0.3 <sup>b</sup>	0.9 <sup>a</sup>	0.007 <sup>a</sup>			
	Min	22.0	13.1	0.3	0.9	0.1	0.2	0.0			
	Max	167.7	1596.1	0.7	8.7	0.5	7.5	0.02			
E3	Mean	54.3	100	0.6	1.5	0.4	0.6	0.002	50	30	20
	Median	41.6 <sup>b</sup>	31.3 <sup>ab</sup>	0.5 <sup>a</sup>	1.0 <sup>a</sup>	0.3 <sup>a</sup>	0.1 <sup>b</sup>	0.0 <sup>bc</sup>			
	Min	31.6	13.3	0.5	0.7	0.2	0.0	0.0			
	Max	122.6	509.5	1.0	4.5	0.8	3.2	0.04			
E4	Mean	50.8	152	0.6	1.6	0.4	0.6	0.004	45	34	21
	Median	43.9 <sup>ab</sup>	25.0 <sup>abc</sup>	0.5 <sup>ab</sup>	1.0 <sup>a</sup>	0.4 <sup>b</sup>	0.2 <sup>b</sup>	0.0 <sup>c</sup>			
	Min	23.3	1.5	0.4	0.7	0.3	0.0	0.0			
	Max	135.8	856.2	0.8	4.2	0.7	2.7	0.02			
Baseflow	Mean	22.9	9.3	0.6	1.1	0.4	0.1	0.002	54	36	9
	Median	20.2 <sup>a</sup>	7.0 <sup>c</sup>	0.6 <sup>ab</sup>	1.0 <sup>a</sup>	0.4 <sup>ab</sup>	0.1 <sup>b</sup>	0.0 <sup>c</sup>			
	Min	19.4	5.8	0.4	0.9	0.2	0.0	0.0			
	Max	32.0	17.5	0.7	1.4	0.6	0.2	0.03			

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4 692 **Table 3** Pearson correlation coefficients (r) between discharge-weighted mean  
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6 693 concentrations of SS and N and rainfall condition during the rising limb of discharge in  
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8 694 each storm events  
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Storm event	r value for the N concentration and rainfall intensity				r value for the N concentration and accumulative rainfall			
	SS	NO <sub>3</sub> -N	DON	PN	SS	NO <sub>3</sub> -N	DON	PN
E1	-0.768**	-0.724*	-0.807**	-0.622	0.893**	0.882**	0.768**	0.768**
E2	-0.794**	-0.282	-0.702*	-0.713*	0.881**	0.865**	0.928**	0.912**
E3	-0.323	-0.307	-0.583	-0.426	0.741*	0.784*	0.912**	0.812*
E4	-0.177	-0.038	-0.146	-0.162	0.871**	0.898**	0.879**	0.878**

\*\*P<0.01; \*p<0.05

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696 **Table 4** Summary statistics for regressions describing the exponential decline ( $k$ ) in the  
 697 concentrations of N during storm events

	Storm event	$k$ ( $\text{h}^{-1}$ )	$r^2$	Time constant $t_{1/e}$ (h)
SS	E1	$-0.039 \pm 0.007$	$0.72 \pm 0.48$	$25.87 \pm 3.93$
	E2	$-0.071 \pm 0.007$	$0.89 \pm 0.48$	$14.01 \pm 1.26$
	E3	$-0.203 \pm 0.022$	$0.84 \pm 0.49$	$4.92 \pm 0.49$
	E4	$-0.463 \pm 0.122$	$0.67 \pm 0.94$	$2.16 \pm 0.45$
	Average	$-0.194 \pm 0.039$	$0.78 \pm 0.59$	$11.74 \pm 1.53$
$\text{NO}_3^-$ -N	E1	$-0.010 \pm 0.001$	$0.90 \pm 0.06$	$97.35 \pm 9.00$
	E2	$-0.038 \pm 0.005$	$0.81 \pm 0.09$	$26.10 \pm 3.13$
	E3	$-0.036 \pm 0.010$	$0.53 \pm 0.14$	$27.48 \pm 6.11$
	E4	$-0.063 \pm 0.016$	$0.66 \pm 0.15$	$15.86 \pm 3.20$
	Average	$-0.037 \pm 0.008$	$0.72 \pm 0.11$	$41.70 \pm 5.36$
DON	E1	$-0.019 \pm 0.002$	$0.84 \pm 0.15$	$52.64 \pm 6.08$
	E2	$-0.083 \pm 0.012$	$0.78 \pm 0.20$	$12.00 \pm 1.52$
	E3	$-0.081 \pm 0.012$	$0.82 \pm 0.16$	$12.39 \pm 1.55$
	E4	$-0.156 \pm 0.019$	$0.93 \pm 0.10$	$6.43 \pm 0.72$
	Average	$-0.085 \pm 0.011$	$0.84 \pm 0.15$	$20.87 \pm 2.47$
PN	E1	$-0.035 \pm 0.005$	$0.79 \pm 0.33$	$28.29 \pm 3.67$
	E2	$-0.245 \pm 0.018$	$0.94 \pm 0.29$	$4.09 \pm 0.27$
	E3	-	-	-
	E4	-	-	-
	Average	$-0.139 \pm 0.011$	$0.86 \pm 0.31$	$16.19 \pm 1.97$

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**Table 5** MFF<sub>30</sub> and MFF<sub>50</sub> for quantifying the magnitude of first flush

Storm event	MFF <sub>30</sub>					MFF <sub>50</sub>				
	NO <sub>3</sub> -N	DON	TN	PN	SS	NO <sub>3</sub> -N	DON	TN	PN	SS
E1	1.13	1.23	1.50	1.87	2.17	1.14	1.22	1.34	1.54	1.64
E2	1.20	1.37	1.90	2.17	2.30	1.14	1.30	1.60	1.74	1.82
E3	1.20	1.37	1.77	2.87	2.50	1.12	1.28	1.40	1.72	1.88
E4	1.17	1.27	1.37	1.87	2.43	1.10	1.26	1.24	1.42	1.66

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**Table 6** N loads during storm events and percentage of annual load

	Load (kg)					% of annual load				
	SS	TN	NO <sub>3</sub> -N	DON	PN	SS	TN	NO <sub>3</sub> -N	DON	PN
E1	396.4	18.3	6.3	3.3	8.6	0.5	1.7	1.3	1.4	2.3
E2	25196.8	168.4	24.9	17.9	125.0	29.3	15.5	5.3	7.7	34.0
E3	3014.8	56.9	23.6	15.6	17.9	3.5	5.2	5.0	6.7	4.9
E4	3342.9	58.0	21.7	20.7	15.6	3.9	5.3	4.6	8.9	4.2
Total	31950.9	301.6	76.5	57.5	167.1	37.2	27.7	16.2	24.7	45.4

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For review

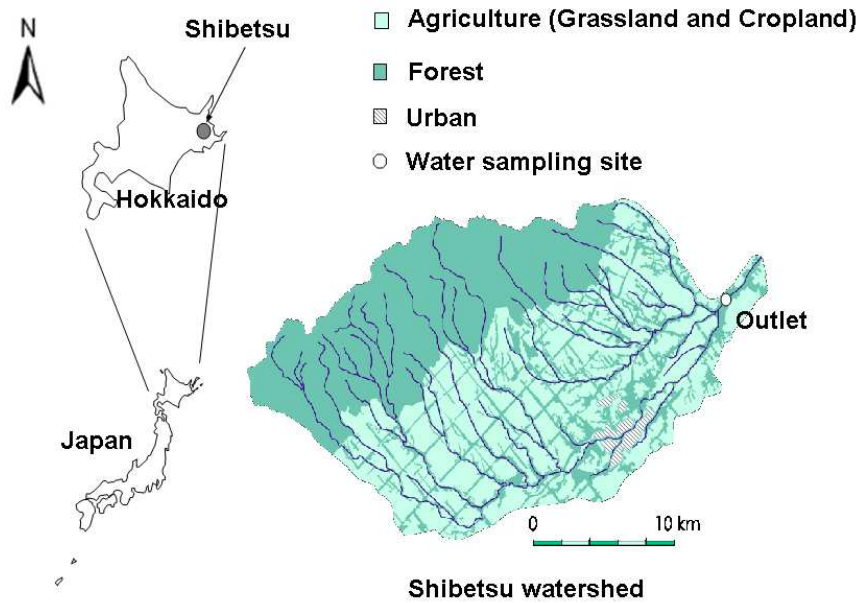


figure 1 Location of the study watershed and water sampling site  
254x190mm (96 x 96 DPI)

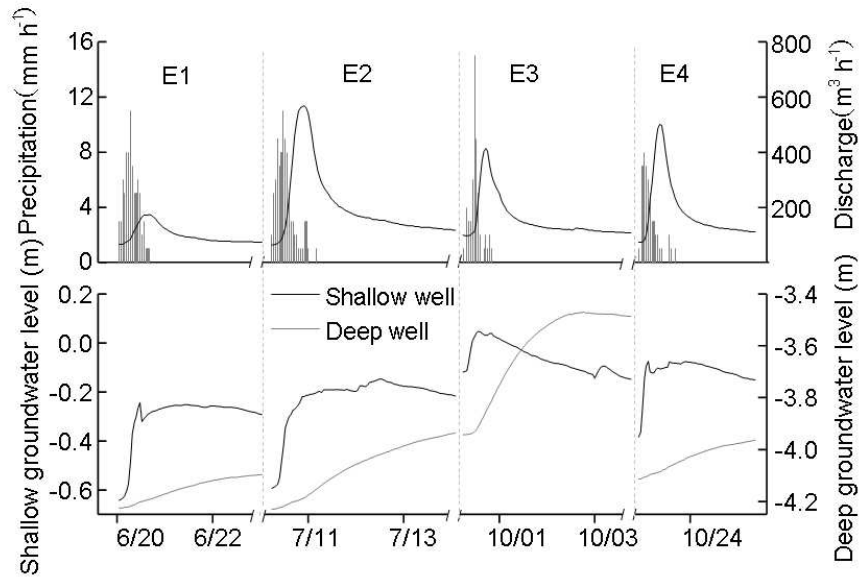


figure 2 Precipitation, stream discharge, and ground water level (only one well is shown, the others are similar) during storm events in 2003  
254x190mm (96 x 96 DPI)

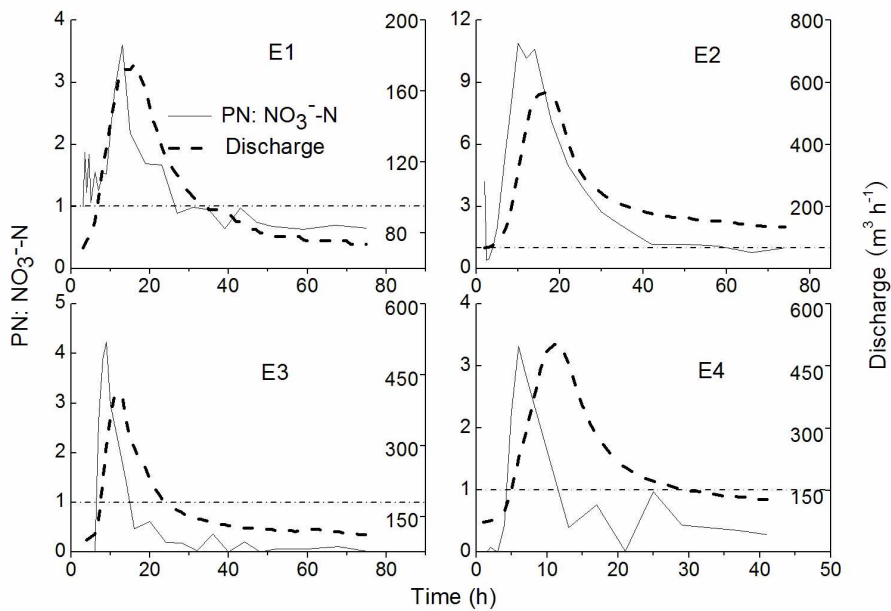
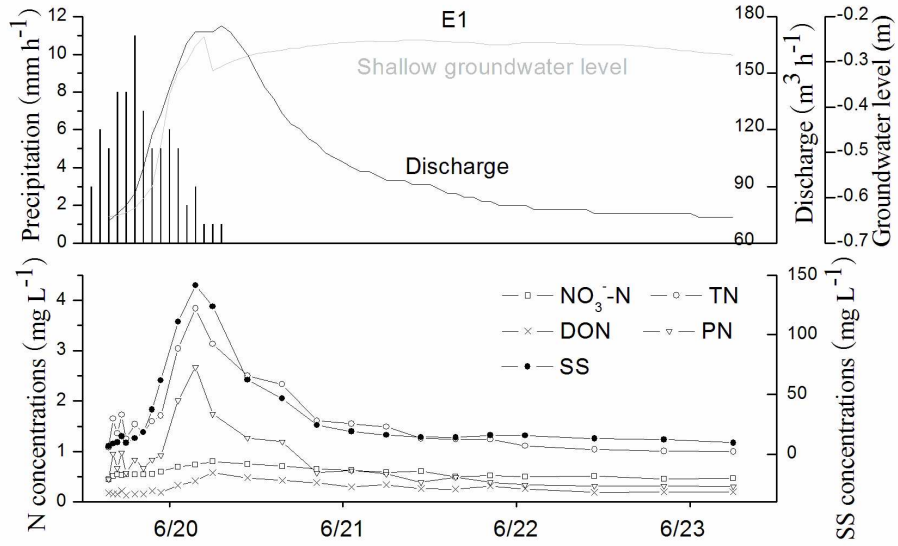
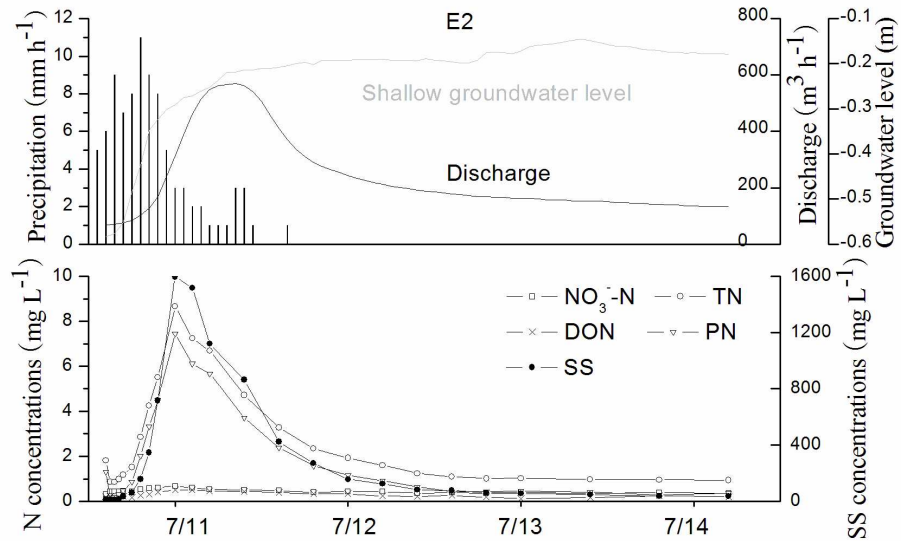


figure 3 The ratio of PN: NO<sub>3</sub><sup>-</sup>-N during storm events  
284x201mm (150 x 150 DPI)



311x198mm (150 x 150 DPI)

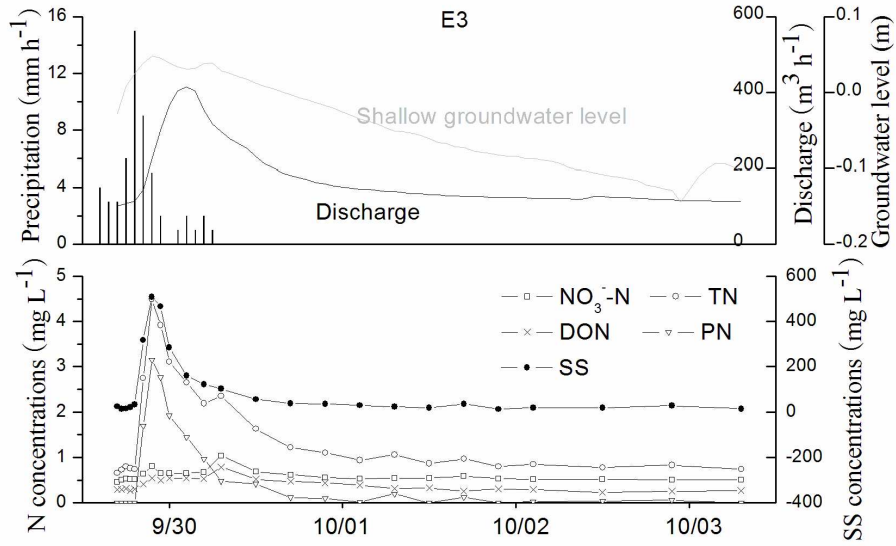
Review



312x202mm (150 x 150 DPI)

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311x202mm (150 x 150 DPI)

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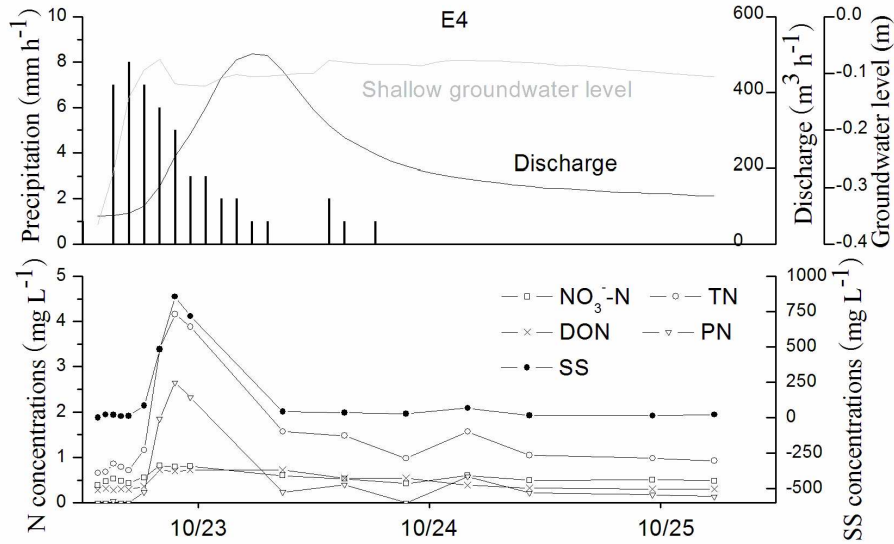
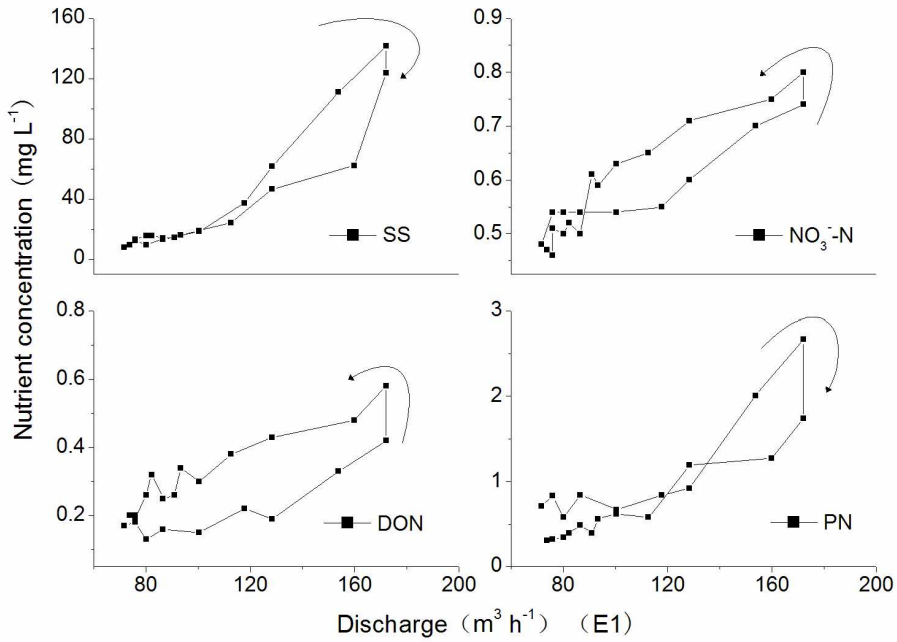
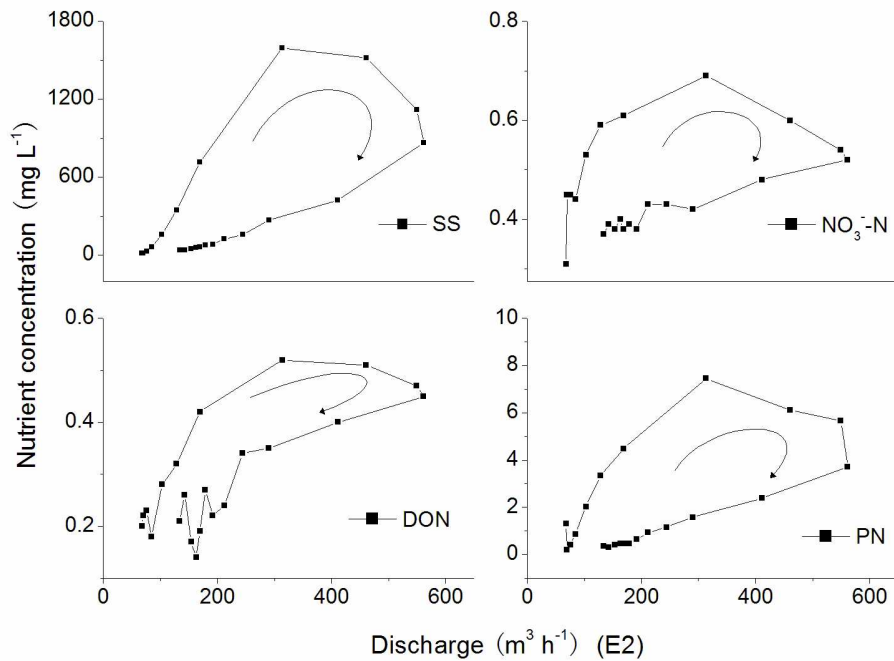


figure 4 Temporal changes in N and SS concentrations, discharge, rainfall, and shallow groundwater level during storm events  
311x202mm (150 x 150 DPI)



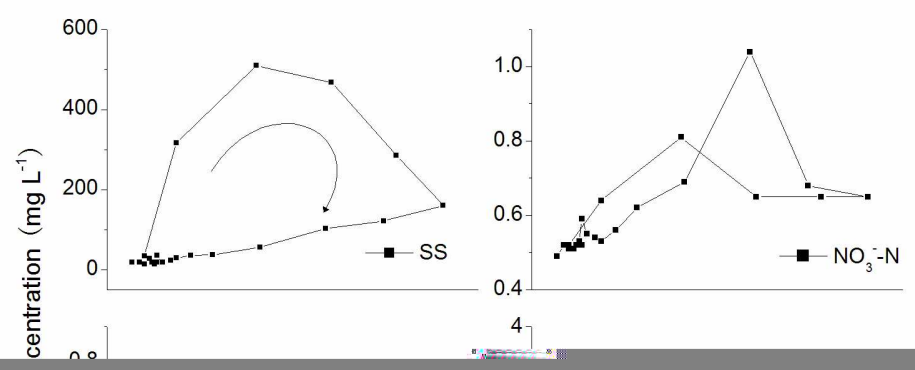
275x204mm (150 x 150 DPI)

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271x207mm (150 x 150 DPI)

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271x203mm (150 x 150 DPI)

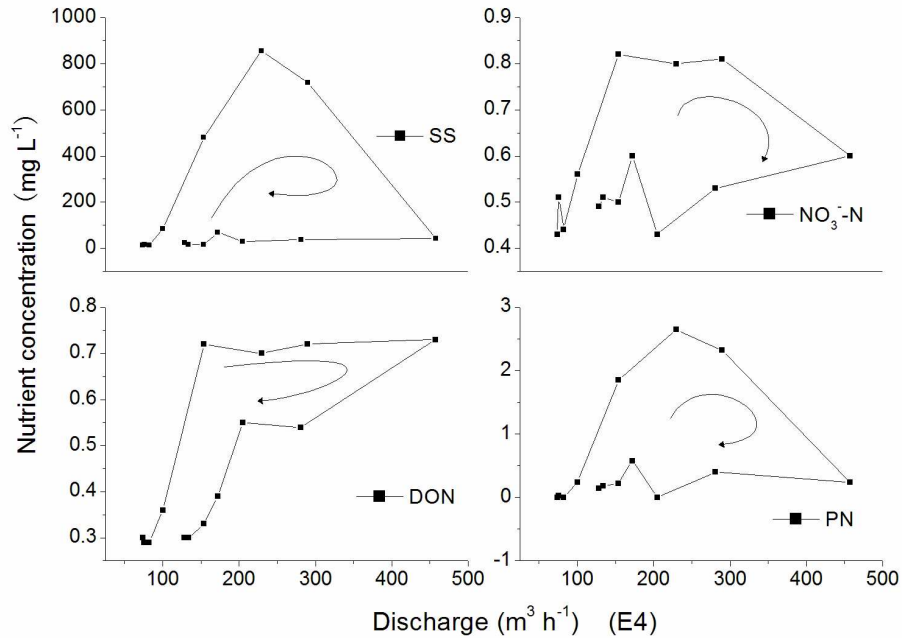


figure 5 Patterns of N and SS during storm events. Arrows indicate the time course  
278x206mm (150 x 150 DPI)

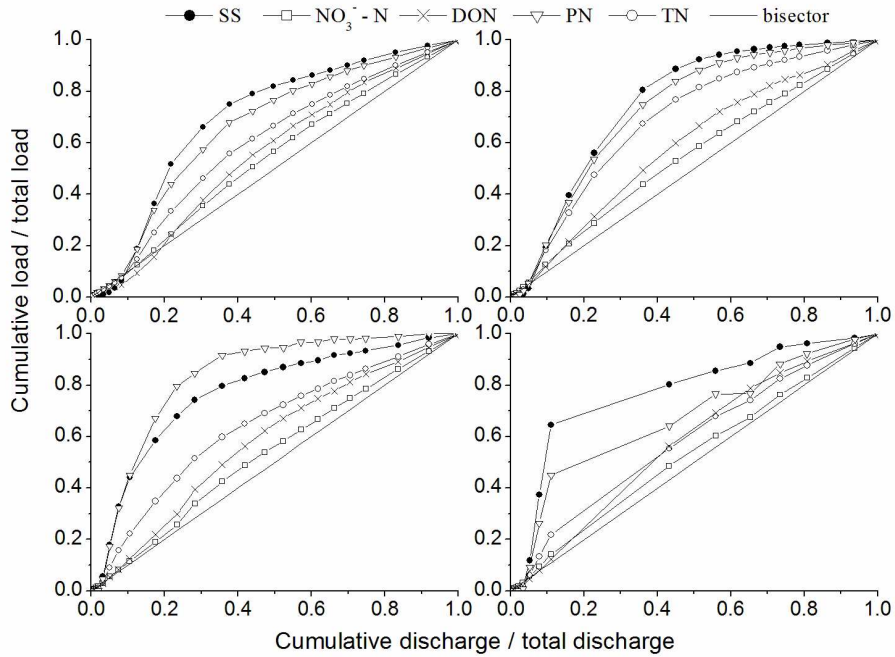


figure 6 M (V) curve: normalized mass first flush relative to normalized discharge  
274x209mm (150 x 150 DPI)

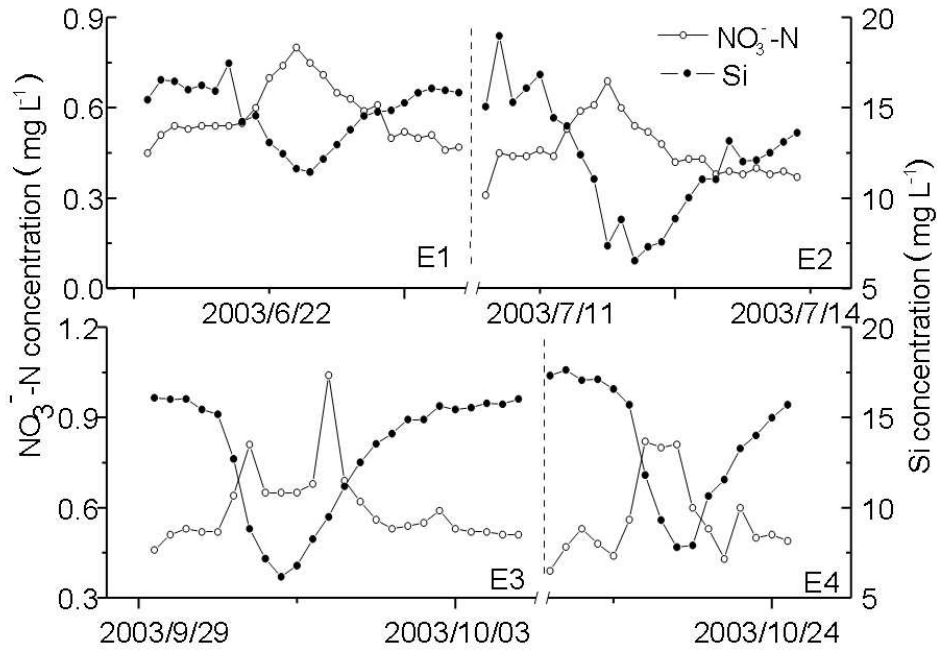


figure 7 Concentrations of Si and  $\text{NO}_3^-$ -N during storm events  
254x190mm (96 x 96 DPI)

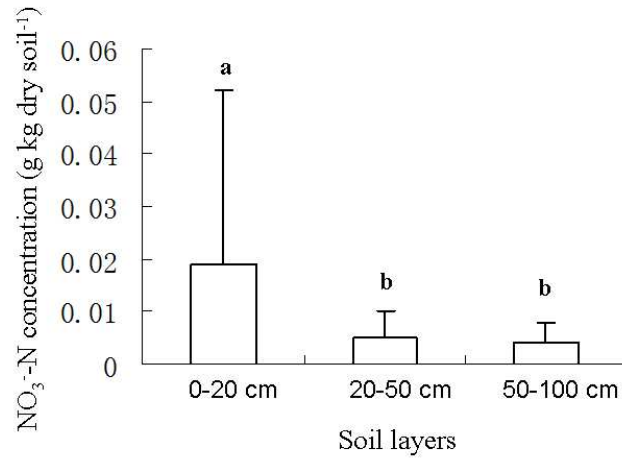


figure 8  $\text{NO}_3^-$ -N concentrations in soil profile (ANOVA,  $p < 0.05$ ,  $n = 27$ )  
254x190mm (96 x 96 DPI)

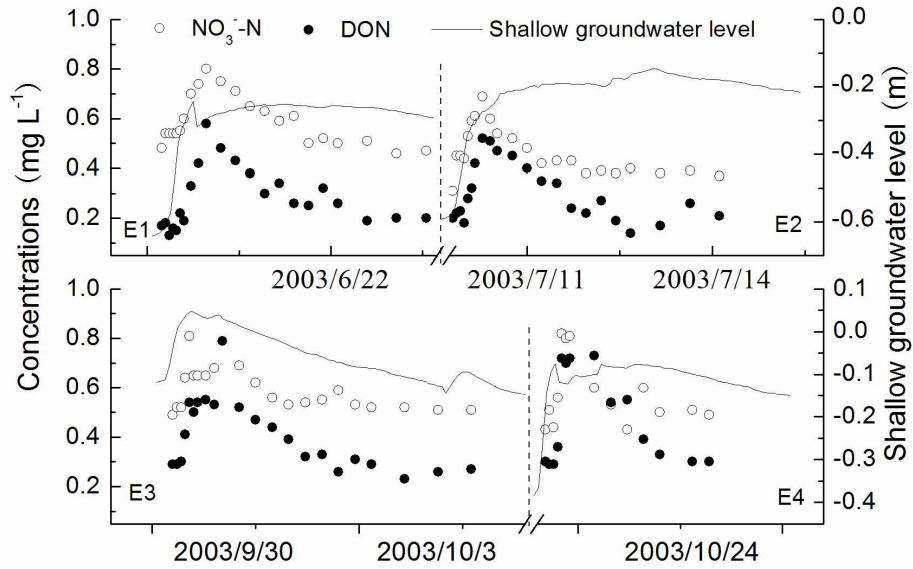


figure 9 Concentrations of  $\text{NO}_3^-$ -N and DON, and shallow ground water level during storm events  
312x207mm (150 x 150 DPI)